

PATENT SPECIFICATION

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(54) METHOD OF SIZING PAPER

- (71) We, RÖHM G.M.B.H. a German Body Corporate of Darmstadt, Germany, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—
- The present invention relates to a novel method of sizing paper using a cationic dispersion of a synthetic resin.
- It has previously been proposed to use synthetic resin dispersions in place of colophony or other natural binders for the sizing of paper pulp and paper surfaces. Originally anionic synthetic resin dispersions were used for this purpose although they have the disadvantage that they do not readily adhere to the paper fibres and are only coagulated and deposited on the fibres by using precipitants. Moreover, the retention of the resin during sheet formation was unsatisfactory despite the use of precipitants. As is known the surface of cellulose fibres is negatively charged in aqueous suspension so that it was desirable to use cationic resin dispersions which due to the opposite charges could be attached to the fibre surface without further measures being necessary. However, these cationic resin dispersions proved to be much less stable than anionic or non-ionic dispersions. Difficulties therefore occurred during the production and storage of the cationic dispersions and particularly during working into the paper pulp or during processing on the sizing press. Furthermore, the limited shearing strength of the dispersions led to annoying deposits on all rapidly moving machine parts which came into contact with the dispersion particles.
- An improvement in this field was obtained by introducing cationic groups into the synthetic resin. In the case of resins of vinyl monomers this was achieved, for example, by copolymerising such monomers with quaternary vinyl imidazolium salts or esters of acrylic or methacrylic acid having a quaternary ammonium grouping in the alcohol moiety. Although the stability of such dispersions was relatively good, they did however suffer from the disadvantage that they did not adhere satisfactorily to the paper fibres which is disadvantageous not only in view of the loss of binder but in particular in view of the resulting sewage problems.
- It has also been proposed to produce dispersions of this type containing units of N-methylol acrylamide or methacrylamide. These dispersions when introduced into paper, cross-link at temperatures of 120 to 160°C and therefore raise the thermoplasticity of the plastic. This has the advantage that papers finished with such dispersions can be allowed to pass over hot rollers during the manufacturing process without any great risk of sticking. In addition such papers are not sensitive to the organic solvents contained in printing inks or adhesives. However, it has hitherto been preferred to avoid the danger of the paper sticking to the hot rollers by adding starch to the surface sizing mixtures although these auxiliary substances can only be used with limited success in pulp sizing. Unfortunately the use of self-cross-linking dispersions of the above-described type has the disadvantage that the resins do not adhere so well to paper fibres as other thermoplastic dispersions i.e. there are even greater binder losses and sewage problems.
- It is an object of the present invention to provide a new and advantageous method of sizing paper using a dispersion of a synthetic resin.
- This new method has been made possible as a result of new knowledge regarding the deposition process of resin dispersion particles on cellulose fibres.
- While we do not wish to be limited by any particular theory, we believe that the presence of cationic groups in the polymer increases the difficulty of depositing the

dispersion particles on the fibre surface as a result of two factors. The first factor is based on the charges themselves whereby the greater the number of cationic charges per unit weight of the dispersed resin the sooner the negative charges of the fibre surface become saturated. When the extent of resin deposition exceeds the saturation point of the fibre surface, the latter becomes cationically charged and therefore repels further resin particles. The second factor is due to the hydrophilicity of the quaternary ammonium group and is increased by further hydrophilic groups. Resin particles with a number of strongly hydrophilic groups are so strongly dispersed and hydrated in an aqueous medium, even in the absence of emulsifiers, that they have no noteworthy tendency to be deposited from the dispersed state onto a surface. Resin particles which contain not only cationic groups but also carboxyl group, hydroxyl groups, carbonamide groups or amide methylol groups or other hydrophilic groups in the polymer are therefore particularly difficult to deposit on a cellulose fibre surface in quantities larger than the charge equivalent. This applies to the above-mentioned self-cross-linking plastics dispersions with cationic groups. On the basis of this knowledge, we have produced dispersions of resins which are as little hydrophilic as possible, the dispersions having a cationic character provided solely by the use of cationic surface active agents, the necessary stability of the dispersions was achieved by the use of non-ionic emulsifiers.

According to one feature of the present invention we provide a method of sizing paper which comprises treating paper pulp or the surface of a paper web with a cationic aqueous dispersion of a non-ionic synthetic resin which is capable of self-cross-linking at temperatures of more than 100°C, the cationic character of the dispersion being provided by the presence of at least one cationic surface active agent in the dispersion, the dispersion further containing at least one non-ionic emulsifying agent.

From experiments which we have carried out, we have found that the method according to the present invention can be used to effect sizing of paper wherein the size adheres uniformly and firmly to the paper without the use of precipitants. In our new sizing method, we have found that sheet formation of the size composition within the paper is reduced or eliminated and processing on hot rollers does not cause sticking of the paper web even if the resin is used in a relatively high concentration. Finally, in our experiments, we have found that the sized papers obtained by the method according to the invention are generally insensitive, to a considerable

extent, to water, dilute acids or alkalis, as well as organic solvents.

The cationic character of the dispersions used in the method according to the invention can be kept sufficiently small such that neutralisation of the anionic charges on the cellulose surface still does not occur with a low charge on the resin. In spite of this, a loss of stability of the dispersed resin particles does occur as a result of charge neutralisation such that the resin particles are completely deposited on the fibre surface. By cross-linking at temperatures of for example 120 to 160°C the resin may be generally converted into a state wherein it neither sticks to hot rollers nor is it soluble in organic solvents or dilute acids or alkalis.

The term "non-ionic" when used herein in relation to the synthetic resins indicates those resins which do not contain appreciable quantities of any groups bound to the macromolecule which are converted into dissociated salts in neutral, acid or alkaline aqueous media. The proportion of such groups, which may occur in small amounts in industrially produced materials as a result of impurities in the starting material, must be kept sufficiently low so that the resin particles are neither soluble nor swellable in neutral, acid or alkaline aqueous media and do not remain in the dispersed state in the absence of an emulsifier.

The dispersed resins employed in the method according to the invention are preferably vinyl polymers obtained by free radical polymerisation of ethylenically unsaturated monomers in aqueous emulsion. Particularly preferred resins are those composed of 70 to 99.5% by weight of units of an ester of acrylic and/or methacrylic acid or a mixture thereof with units of vinylidene chloride or styrene and/or a homologue thereof; 0.5 to 12% by weight of units of at least one N-methylol amide or a N-methylol ether amide of acrylic or methacrylic acid; and if desired, up to 29.5% by weight of units of one or more other non-ionic copolymerisable monomers. The monomers of the first-mentioned group generally have the greatest influence on the mechanical characteristics of the resins. These monomers include those which impart hardness to the resins and a high softening temperature, in particular methyl methacrylate, styrene and its homologues such as vinyl toluene or α -methyl-styrene and to a lesser extent ethyl, propyl and butyl-methacrylate, methylacrylate or vinylidene chloride. The hardness and softening temperature of the resin can be reduced by the use of esters of acrylic acid with 2 or more carbon atoms in the alcohol residue and esters of methacrylic acid with 5

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or more carbon atoms in the alcohol residue. By suitable mixing of monomers which increase the hardness or softness polymers with the exactly desired mechanical characteristics can be produced. For pulp sizing resins are preferably used which in the cross-linked state have a softening temperature (t_{max}) in the range -40 to 25°C . For surface sizes, the hardness and softening temperature are generally somewhat higher e.g. in the range -25 to 40°C .

The thermal cross-linkability of the resins is preferably based on the content of units of methylol amides or methylol ether amides of acrylic and/or methacrylic acid. Units with free methylol amide groups are particularly reactive and are therefore preferred as compared with methylol ether amides for example methoxymethylacrylamide or methacrylamide or butoxymethylacrylamide or methacrylamide. Although these units can react with one another accompanied by cross-linking frequently other monomer components are added to the resin which facilitate the cross-linking reaction. Among these are units of acrylamide or methacrylamide or a hydroxyalkyl ester of acrylic or methacrylic acid such as hydroxyethyl acrylate or methacrylate, 2-hydroxypropyl acrylate or methacrylate or 4-hydroxybutyl acrylate or methacrylate. The total quantity of monomer units which participate in the cross-linking reaction is fixed according to the degree of cross-linking necessary. Units of at least one N-methylol amide or N-methylol ether amide of acrylic or methacrylic acid can for example represent 0.5 to 12%, preferably 1 to 6%, by weight of the polymer. The quantity of the other monomer units which participate in the cross-linking reaction can be of the same order of magnitude but the proportion of these monomers in the resin is kept as low as possible so as to ensure a low hydrophilicity.

Examples of monomers which can be incorporated into the synthetic resin, in addition to the above-mentioned components, in a quantity of up to 29.5% by weight include acrylo and methacrylonitrile, vinyl chloride, vinyl esters such as vinyl acetate or vinyl propionate or olefines such as ethylene, propylene, isobutylene, butadiene or isoprene. The dispersions used in the method according to the invention preferably however contain no such monomer units.

The hydrophilicity or hydrophobicity of the dispersed resins, and thus their tendency to become attached to the paper fibres, is substantially influenced by the ratio of hydrophilic to hydrophobic monomer components. Among the monomers in

question methylol amides as well as the free amides and hydroxy alkyl esters have the highest hydrophilicity. If they are only used in small amounts then the resin particles behave in a substantially hydrophobic manner. With an increase in content of hydrophilic monomer components the hydrophilicity of the resin particles increases unless this is counteracted by the simultaneous incorporation of monomers which tend to give strongly hydrophobic characteristics. Styrene and its homologues as well as esters of acrylic and methacrylic acid with 6 or more C-atoms in the alcohol residue have a hydrophobising action. Since these esters also have a softening effect they can only generally be used in small amounts in view of the necessary hardness and softening temperature. However, styrene and its homologues simultaneously increase the hydrophobic characteristics as well as the hardness and softening temperature of the polymers.

The above-mentioned cationic surface active agent may be for example a C_{12} to C_{14} fatty amine hydrochloride, coconut amine hydrochloride or cetyl trimethyl ammonium chloride. These surface active agents can be used for example in an amount of 0.5 to 2.5% by weight of the aqueous phase. For an effective stabilization of the dispersion the cationic surface active agent is generally not sufficient and is supplemented by one or more non-ionic emulsifiers in quantities of for example 1 to 4% by weight based on the weight of the aqueous phase. Preferred non-ionic emulsifiers include on the one hand those with a surfactant character such as ethoxylated fatty acids, fatty alcohols or alkyl phenols and on the other hand water-soluble protective colloids such as polyvinyl alcohol, polyacrylamide, polyvinylpyrrolidone, polyalkyleneoxides as well as block copolymers of ethylene oxide and propylene oxide.

The dispersions employed in the method according to the invention may be generally prepared in conventional manner. For the preparation of dispersions, it should be noted that the use of those initiators which do not introduce strongly hydrophilic starting groups into the polymer molecules has proved advantageous. A preferred initiator is hydrogen peroxide, if desired, in combination with iron salts.

The dispersions may be added to a pulp-water mixture just before sheet formation. In general, within 10 to 20 minutes at room temperature most of the resin particles are attached to the fibres. Complete separation which is a precondition for clear waste water generally requires a little more time at room temperature but can usually be achieved within the indicated times by heating to 30 to 40°C . The danger of foam

formation increases with the length of time between the dispersion addition and sheet formation.

Although the cationically charged dispersion particles are only attached to the surface of the cellulose fibres the fibrous material need not consist only of cellulose, cotton or mechanical wood pulp. Synthetic fibres such as polyamide or polyester fibres can form a considerable proportion e.g. 20% of the fibrous material.

For most types of paper, an addition of less than 30% (dry weight) of dispersed resin calculated on the dry weight of the paper pulp or paper web is usually adequate. For the production of ink-resistant writing papers and packing-proof printing papers, the dispersion is preferably added to the pulp in the pulp engine at the end of beating to a fibre content of 2 to 5% (based on the total weight of the pulp). For producing conventional writing and printing papers, the quantity of the dispersion to be added is conveniently such that the resin proportion based on the dry weight of the fibrous material forms 3 to 6%. The advantage of the good adhesion of the resin used is of particular significance in the production of papers with a high resin content. Preferably therefore the dispersions are added in an amount (calculated on the dry weight of the resin) of at least 10% by weight of the dry weight of the paper pulp or paper web. Such papers are e.g. used in the production of bank notes. With even higher resin contents i.e. more than 20% by weight the products tend to assume more of a resin character and are suitable for example as map papers or decorative papers in the production of laminates in furniture manufacture.

After sheet formation, the paper web produced may be passed into a drying and condensation zone wherein the water contained in the paper layer is evaporated at a temperature of more than 100°C and the cross-linking reaction is initiated. For example temperatures in the range 110 to 150°C may be used. The complete cross-linking and hardening of the resin is generally obtained in the dry portion of the paper machine or by subsequent calendering of the paper web between heated rollers. The temperature of the rollers is higher the shorter the contact time with the paper web and the smaller the quantity of resin precondensed in the drying zone. Roller temperatures between 110 and 180°C are generally convenient at conventional working rates of 50 to 600 m/min.; however, the roller temperature e.g. with higher proportions of cross-linking components in the resin can also reach 200°C and above without there being any danger of the paper web sticking to the roller.

The advantages of the invention can also be utilised to a great extent in the surface sizing of papers. The dispersions if desired in combination with starch, carboxymethyl cellulose or alginate as well as acid-resistant wax emulsions and pigments may be applied to the paper web preferably with the aid of a sizing press and dried and condensed under similar conditions to those already described in relation to pulp sizing. The concentration of the size is variable but is generally between 3 to 10% calculated on the dry weight of the resin. Size application in the case of writing papers amounts to about 2%, in off-set papers about 5% based on the water weight.

The following Examples illustrate the present invention.

Example 1

A. Preparation of the dispersion

An aqueous emulsion of 50 parts by weight of methyl methacrylate, 42 parts by weight of N-butylacrylate, 5 parts by weight of acrylonitrile and 3 parts by weight of N-hydroxymethyl methacrylamide containing in solution 0.95 parts by weight of C_{14} fatty amine hydrochloride and 0.2 parts by weight of hydrogen peroxide (30%) is added dropwise at 85°C. within 4 to 6 hours to an aqueous solution of 0.05 parts by weight of hydrogen peroxide (30%), 0.005 parts by weight of $FeCl_3$ and 0.05 parts by weight C_{14} fatty amine hydrochloride. At the end of polymerisation 4 parts by weight of adduct of iso-nonylphenol and 100 mol of ethyleneoxide are added. A coagulate-free dispersion is obtained with an approx. 50% solids content.

B. Preparation of raw paper for the production of water-proof abrasive papers

A raw paper suitable for the production of water-proof abrasive papers for the car industry and which has a high water penetration time is produced as follows:

Semi-bleached sulphate cellulose having a consistency of 3.5% and a pH value of 7.5 is beaten in a pulper to a freeness of 40° SR and subsequently mixed with a quantity of the above described dispersion such that for 100 parts of cellulose (dry weight) there are 10 parts of the dispersed resin (dry weight). The mixture is diluted to a consistency of 0.5% and supplied to a Fourdrinier machine. The paper web formed is dried at a cylinder temperature of 130°C. to a final moisture content of 3 to 4%. The raw paper weight is 72 g/m².

Example 2

A. Preparation of the dispersion

Under the conditions given in Example 1A an aqueous emulsion of 15 parts by

weight of methyl methacrylate, 80 parts by weight of ethyl acrylate and 5 parts by weight of N-hydroxymethyl methacrylamide containing in dissolved form 0.2 parts by weight of hydrogen peroxide (30%) and 0.7 parts by weight of cetyl trimethyl ammonium chloride is added dropwise to an aqueous solution of 0.05 parts by weight of hydrogen peroxide (30%), 0.005 parts by weight of FeCl₃ and 0.05 parts by weight of cetyl trimethyl ammonium chloride. After adding 4 parts by weight of an adduct of isononylphenol and 100 mol of ethylene oxide a coagulate-free dispersion with approx. 50% solids content is obtained.

B. Preparation of a decorative paper for the furniture industry

A pulp mixture of 1080 kg of bleached sulphite cellulose 1A birch/pine mixed (5:1) and 350 kg of titanium dioxide of the rutile type, having a consistency of 4%, a freeness of 35° SR and a pH value of 6.3 is mixed with 900 kg of the above-described dispersion. Dilution to a consistency of 1.2% is made at the forward end of a Fourdrinier machine. After drying on drying cylinders at 110 to 130°C. a finished paper of 200 g/m² is obtained. The paper can be subsequently printed on, varnished and embossed.

Example 3

A. Preparation of the dispersion

Analogous to Example 1 an aqueous emulsion of 25 parts by weight of methyl methacrylate, 70 parts by weight of N-butylacrylate, 3 parts by weight of N-hydroxymethyl methacrylamide and 2 parts by weight of methacrylamide wherein are dissolved 0.95 parts by weight of C₁₄ fatty amine hydrochloride and 0.2 parts by weight of hydrogen peroxide (30%) are added to an aqueous solution of 0.05 parts by weight of hydrogen peroxide (30%), 0.005 parts by weight of FeCl₃ and 0.05 parts by weight of C₁₄ fatty amine hydrochloride. The dispersion obtained is subsequently mixed with 4 parts by weight of an adduct of isononylphenol and 100 mol of ethylene oxide. A coagulate-free dispersion with an approximately 50% solids content is obtained.

B. Producing a banknote paper

A fibrous mixture of 60% bleached sulphate cellulose, 20% cotton and 20% nylon fibres of 2.2 dtex is beaten to 55° SR with a consistency of 2.7% in a pulper in the presence of 3% (based on the fibre weight) of titanium dioxide, rutile type and 0.6% of a synthetic calcium silicate (Baysical KN). Then the dispersion produced according to A is added in a quantity (based on the dry weight of the resin) of 20% by weight of the dry weight of the fibrous mixture. The

mixture is diluted to 0.5% by weight fibre content and at a pH value of 5.6 is supplied to a cylinder paper machine. After the wet part the paper web passes at 90 to 100°C. over a spool air dryer and a drying cylinder at 130°C. The paper weight is 75 g/m².

WHAT WE CLAIM IS:—

1. A method of sizing paper which comprises treating paper pulp or the surface of a paper web with a cationic aqueous dispersion of a non-ionic synthetic resin which is capable of self-cross-linking at temperatures of more than 100°C., the cationic character of the dispersion being provided by the presence of at least one cationic surface active agent in the dispersion, the dispersion further containing at least one non-ionic emulsifying agent.
2. A method as claimed in claim 1 wherein the said synthetic resin comprises a copolymer containing 70 to 99.5% by weight of units of an ester of acrylic and/or methacrylic acid or a mixture thereof with units of vinylidene chloride, styrene and/or a homologue thereof, 0.5 to 12% by weight of units of at least one N-methylol amide or N-methylol ether amide of acrylic or methacrylic acid; and if desired, up to 29.5% by weight of units of one or more other non-ionic copolymerisable monomers.
3. A method as claimed in claim 2 wherein paper pulp is treated with the said dispersion and wherein the said synthetic resin is capable of cross-linking to form a cross-linked material having a softening temperature (t_{max}) of from -40° to 25°C.
4. A method as claimed in claim 2 wherein the surface of a paper web is treated with the said dispersion and wherein the said synthetic resin is capable of cross-linking to form a cross-linked material having a softening temperature (t_{max}) of from -25° to 40°C.
5. A method as claimed in any of claims 2 to 4 wherein the said copolymer contains 1 to 6% by weight of units of at least one N-methylol amide or N-methylol-ether amide of acrylic or methacrylic acid.
6. A method as claimed in any of claims 2 to 5 wherein the said copolymer contains units of acrylamide or methacrylamide or a hydroxyalkyl ester of acrylic or methacrylic acid.
7. A method as claimed in any of claims 2 to 6 wherein the said copolymer contains units of acrylonitrile methacrylonitrile, vinyl chloride, a vinyl ester or an olefin.
8. A method as claimed in any of the preceding claims wherein the said cationic surface active agent comprises a C₁₂ to C₁₄ fatty amine hydrochloride, coconut amine hydrochloride or cetyl trimethyl ammonium chloride.
9. A method as claimed in any of the

- preceding claims wherein the said cationic surface active agent is employed in an amount of 0.5 to 2.5% by weight of the aqueous phase of the dispersion.
- 5 10. A method as claimed in any of the preceding claims wherein the non-ionic emulsifying agent comprises an ethoxylated fatty acid, fatty alcohol or alkyl phenol.
- 10 11. A method as claimed in any of claims 1 to 9 wherein the non-ionic emulsifying agent comprises a water-soluble protective colloid.
- 15 12. A method as claimed in claim 11 wherein the non-ionic emulsifying agent comprises polyvinyl alcohol, polyacrylamide, polyvinylpyrrolidone, a polyalkylene oxide or a block copolymer of ethylene oxide and propylene oxide.
- 20 13. A method as claimed in any of the preceding claims wherein the non-ionic emulsifying agent is employed in an amount of 1 to 4% by weight of the aqueous phase of the dispersion.
- 25 14. A method as claimed in any of the preceding claims wherein the dispersion is employed in an amount (calculated on the dry weight of the resin) of less than 30% by weight of the dry weight of the paper pulp or paper web.
- 30 15. A method as claimed in any of the preceding claims wherein the dispersion is employed in an amount (calculated on the dry weight of the resin) of at least 10% by weight of the dry weight of the paper pulp or paper web.
16. A method as claimed in any of the preceding claims wherein the said paper web, or a paper web produced from the said paper pulp, is heated to a temperature of more than 100°C. to effect cross-linking of the resin.
17. A method as claimed in claim 16 wherein the said paper web, or a paper web produced from the said paper pulp, is heated to a temperature of 110° to 150°C. to effect cross-linking of the resin.
18. A method as claimed in claim 16 or claim 17 wherein heating is effected by passing the paper web over heated rollers.
19. A method of sizing paper as claimed in claim 1 substantially as herein described.
20. A method of sizing paper substantially as herein described in any of the Examples.
21. Paper whenever sized by a method as claimed in any of the preceding claims.

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